

(12) **United States Patent**
Chi et al.

(10) **Patent No.:** **US 9,406,525 B2**
(45) **Date of Patent:** **Aug. 2, 2016**

(54) **METHOD FOR SEMICONDUCTOR
MANUFACTURING**

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(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 105 days.

(21) Appl. No.: **14/081,630**

(22) Filed: **Nov. 15, 2013**

(65) **Prior Publication Data**

US 2015/0140829 A1 May 21, 2015

(51) **Int. Cl.**
H01L 21/033 (2006.01)
H01L 21/311 (2006.01)
H01L 21/67 (2006.01)

(52) **U.S. Cl.**
CPC **H01L 21/31133** (2013.01); **H01L 21/6708**
(2013.01)

(58) **Field of Classification Search**
USPC 438/725, 748; 216/83, 88, 90; 134/19,
134/34

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,362,682	A *	11/1994	Bozler et al.	438/458
5,931,721	A *	8/1999	Rose et al.	451/89
5,989,354	A *	11/1999	Dormer et al.	134/2
6,204,081	B1 *	3/2001	Kim et al.	438/30
6,273,790	B1 *	8/2001	Neese et al.	451/38
2005/0139487	A1 *	6/2005	Zwicker et al.	205/701
2006/0046482	A1 *	3/2006	Verhaverbeke	438/689
2007/0089761	A1 *	4/2007	Banerjee et al.	134/34
2011/0247661	A1 *	10/2011	Hayashida	H01L 21/67051 134/34
2014/0137892	A1 *	5/2014	Brown et al.	134/18

* cited by examiner

Primary Examiner — Shamim Ahmed

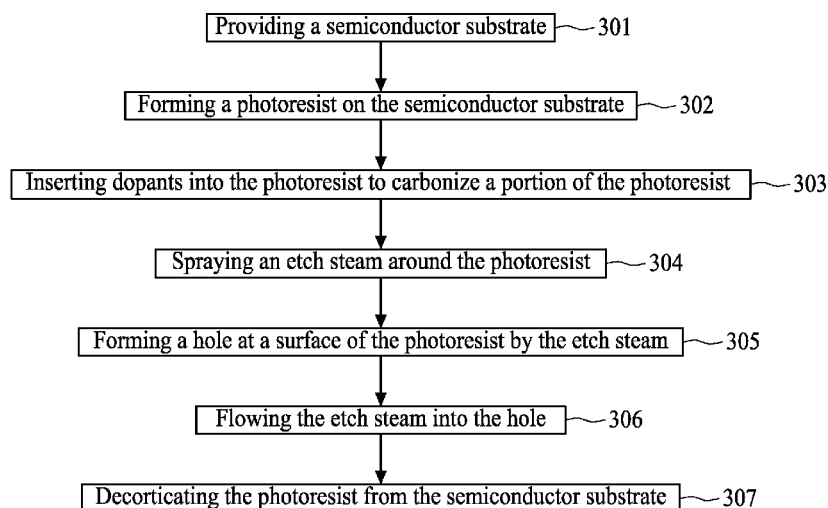
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Property Attorneys; Anthony King

(57) **ABSTRACT**

A method includes followings operations. A semiconductor substrate is provided. A photoresist is formed on the semiconductor substrate. Dopants are inserted into the photoresist to carbonize a portion of the photoresist. An etch steam is sprayed on the semiconductor substrate and the photoresist. A hole is formed at a surface of the photoresist by the etch steam. The etch steam is flowed into the hole so as to remove a portion of the photoresist at an interface between the semiconductor substrate and the photoresist. The photoresist is decorticated from the semiconductor substrate.

20 Claims, 15 Drawing Sheets

300



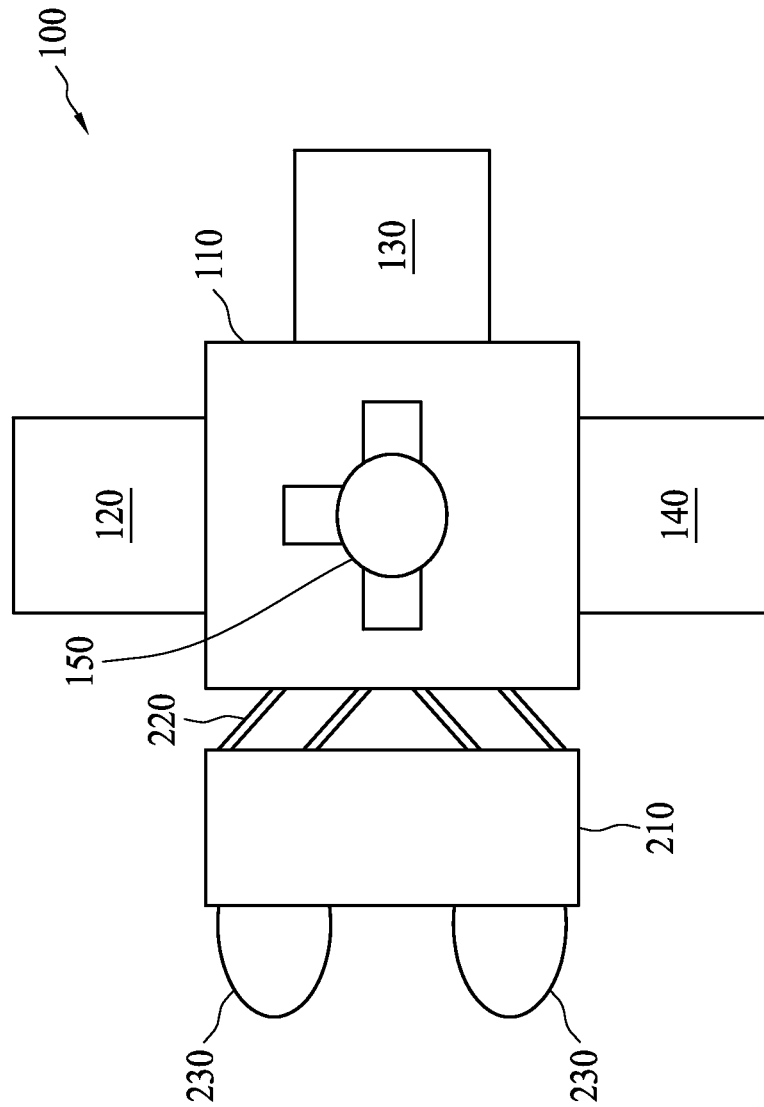


FIG. 1

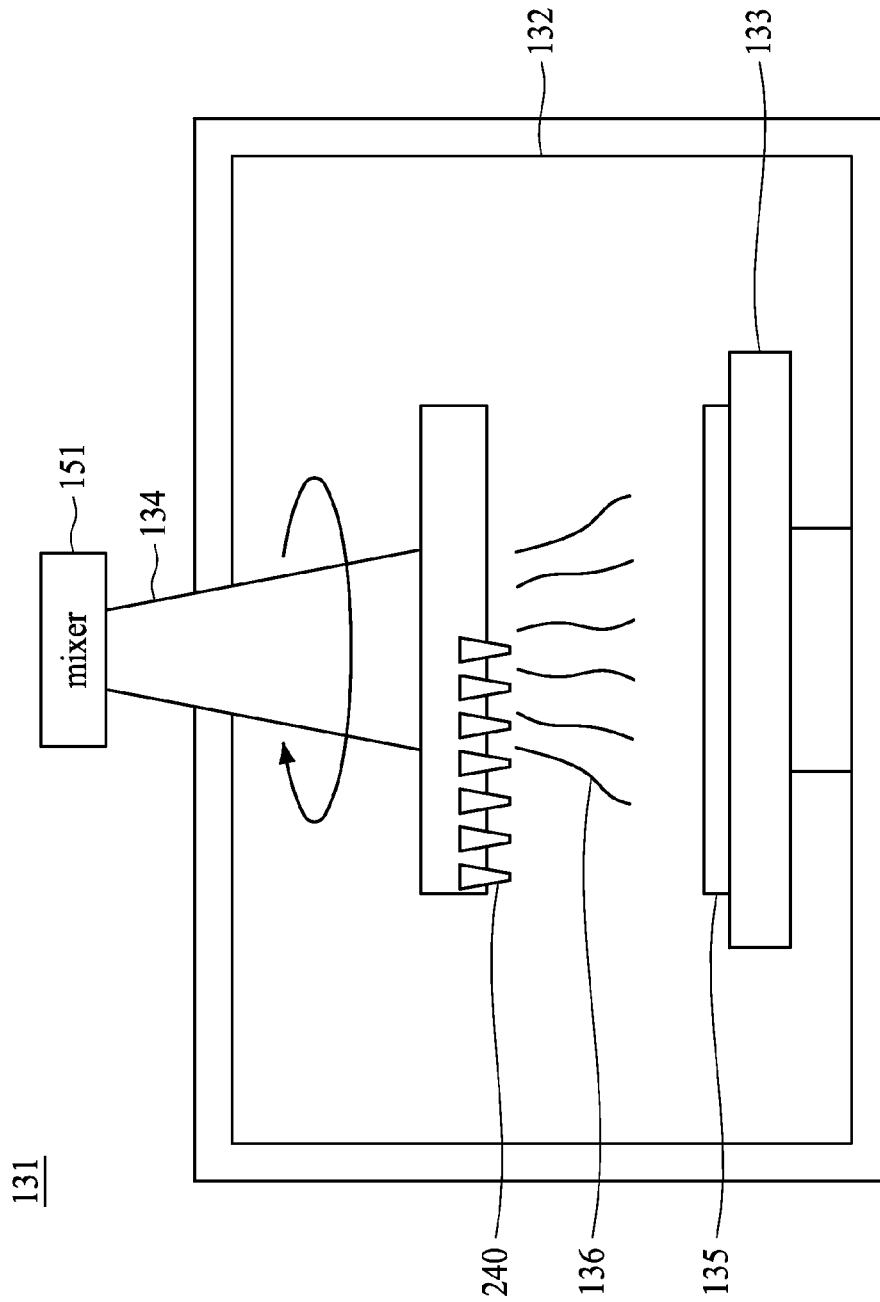


FIG. 2

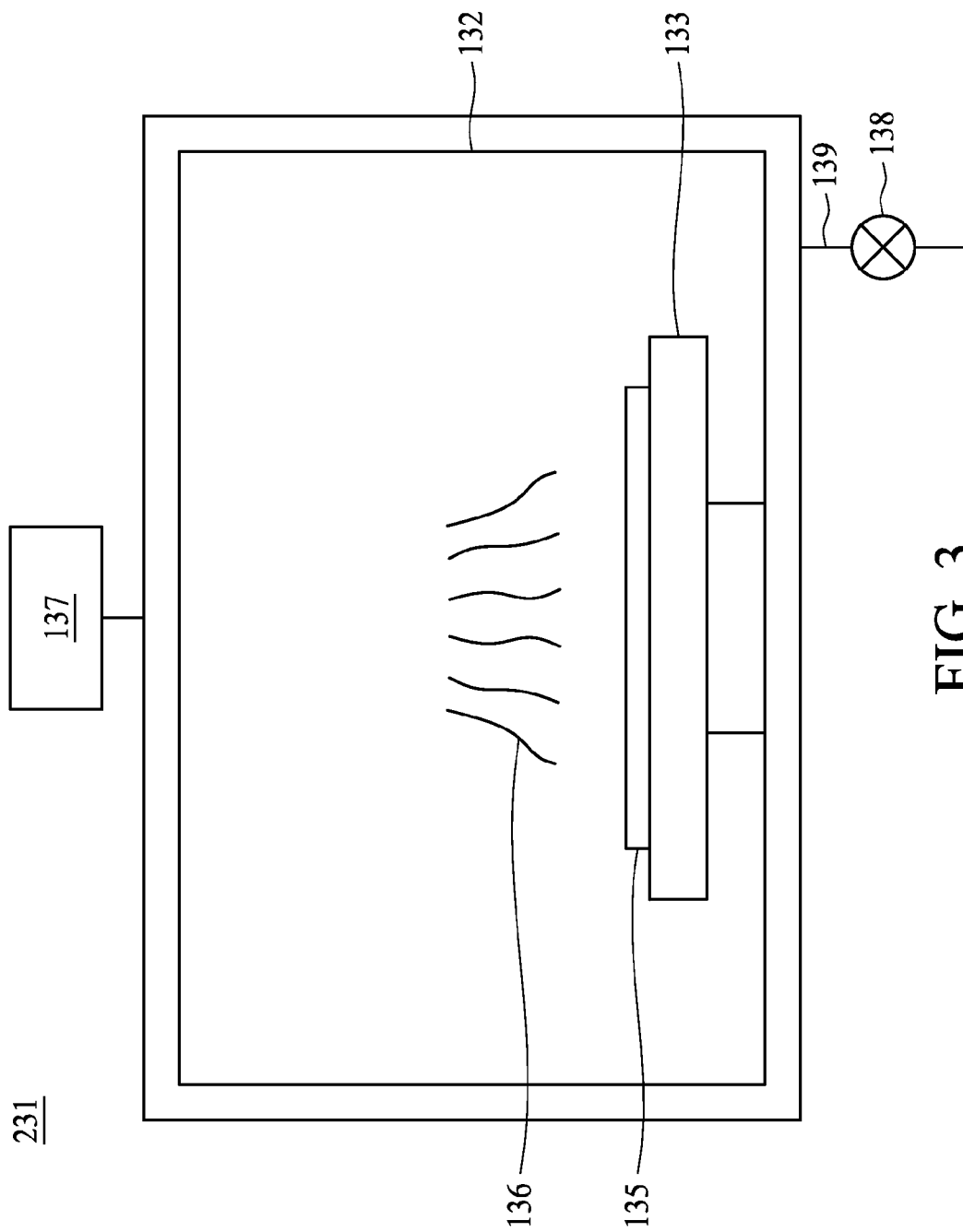


FIG. 3

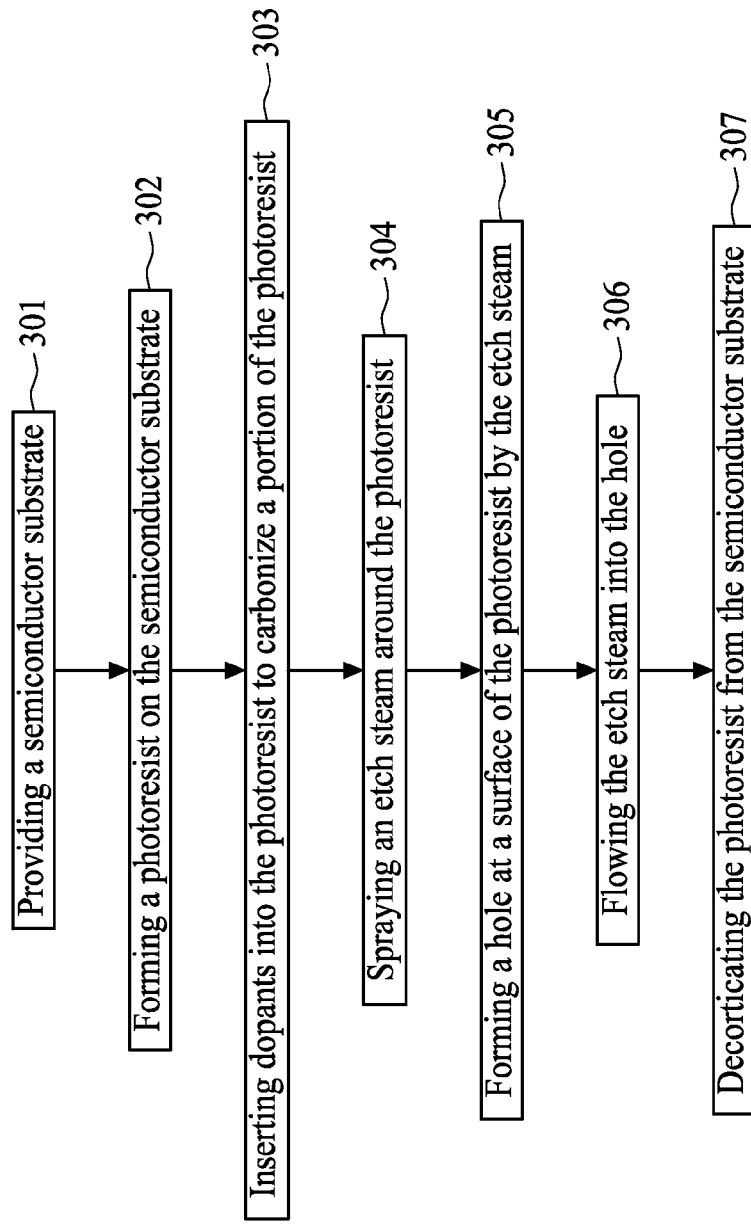
300

FIG. 4

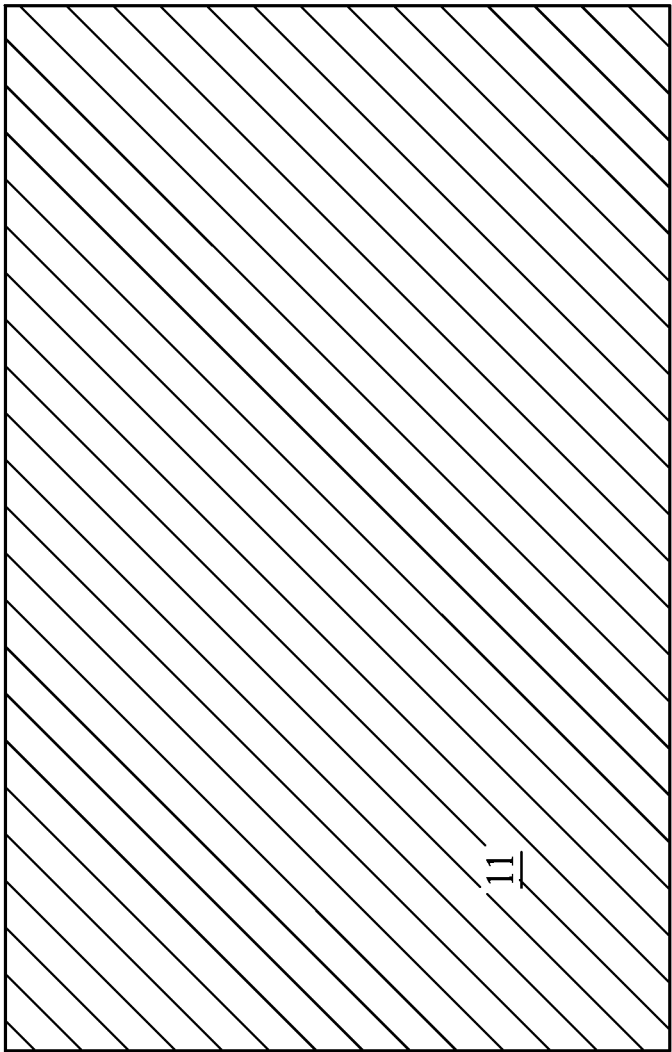


FIG. 5

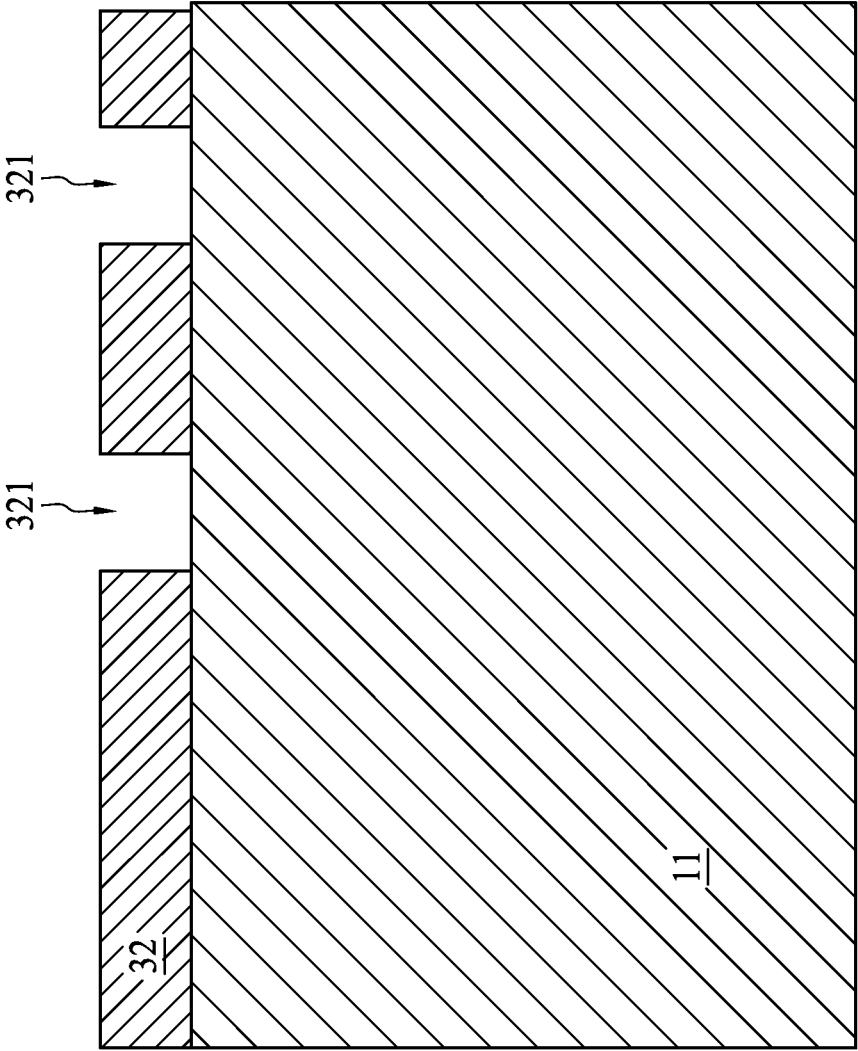


FIG. 6

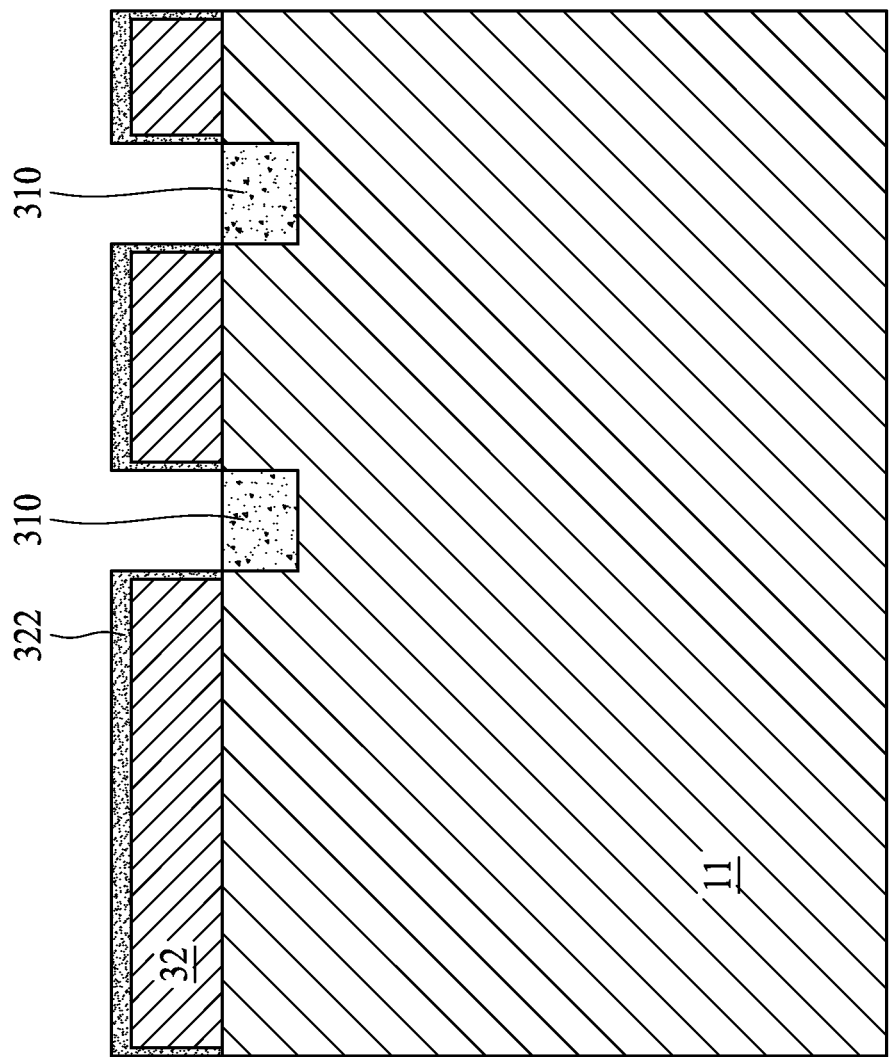


FIG. 7

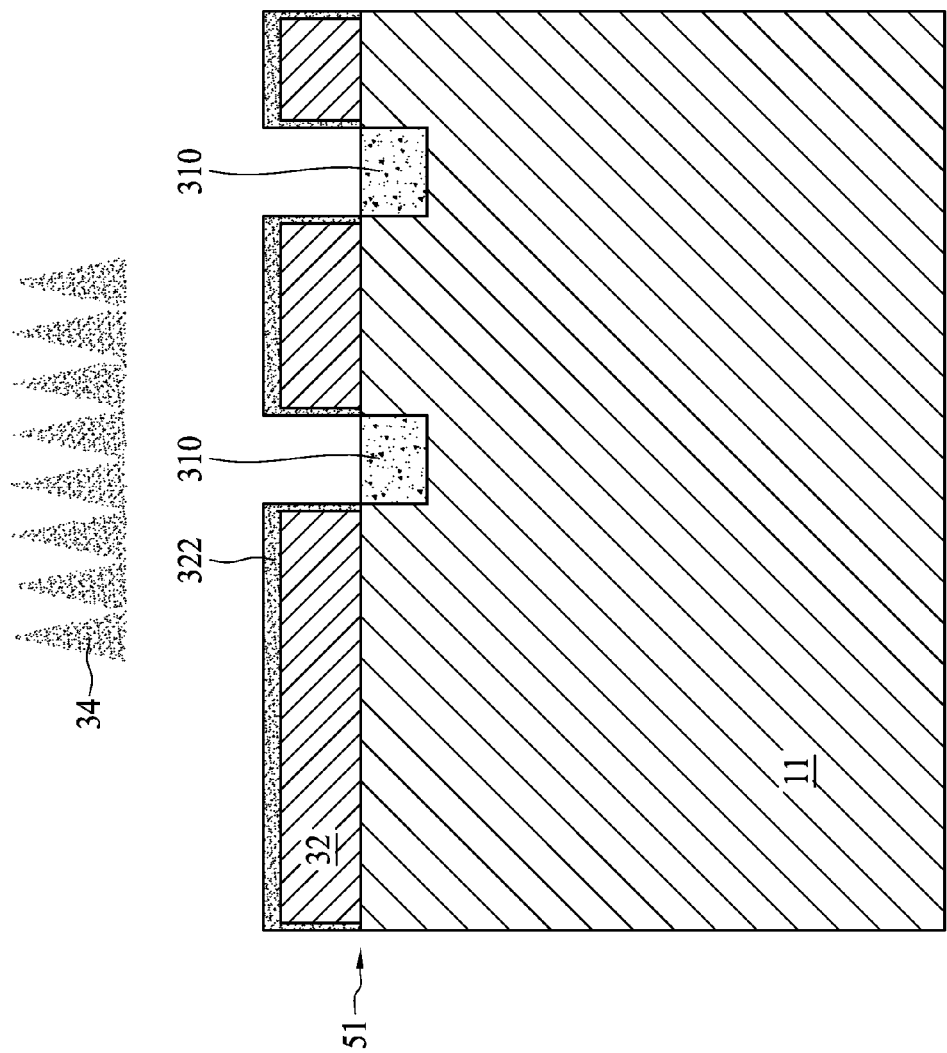


FIG. 8

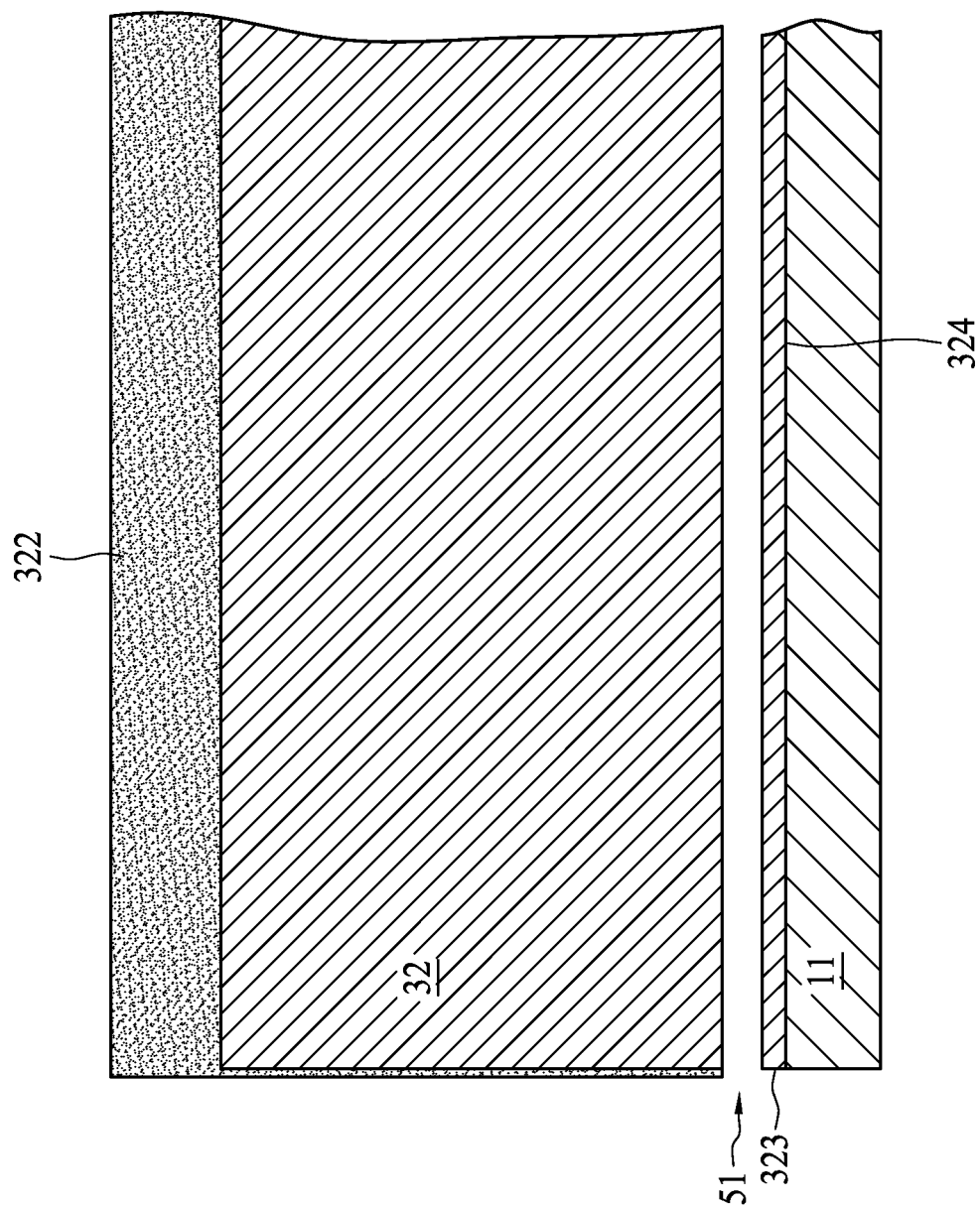


FIG. 9

400

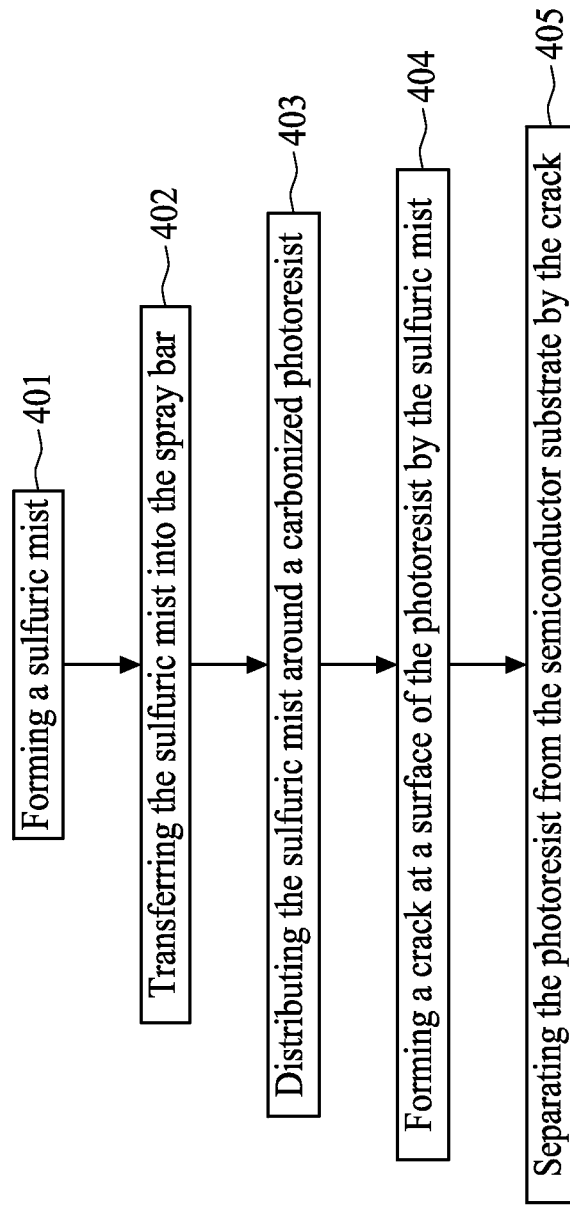


FIG. 10

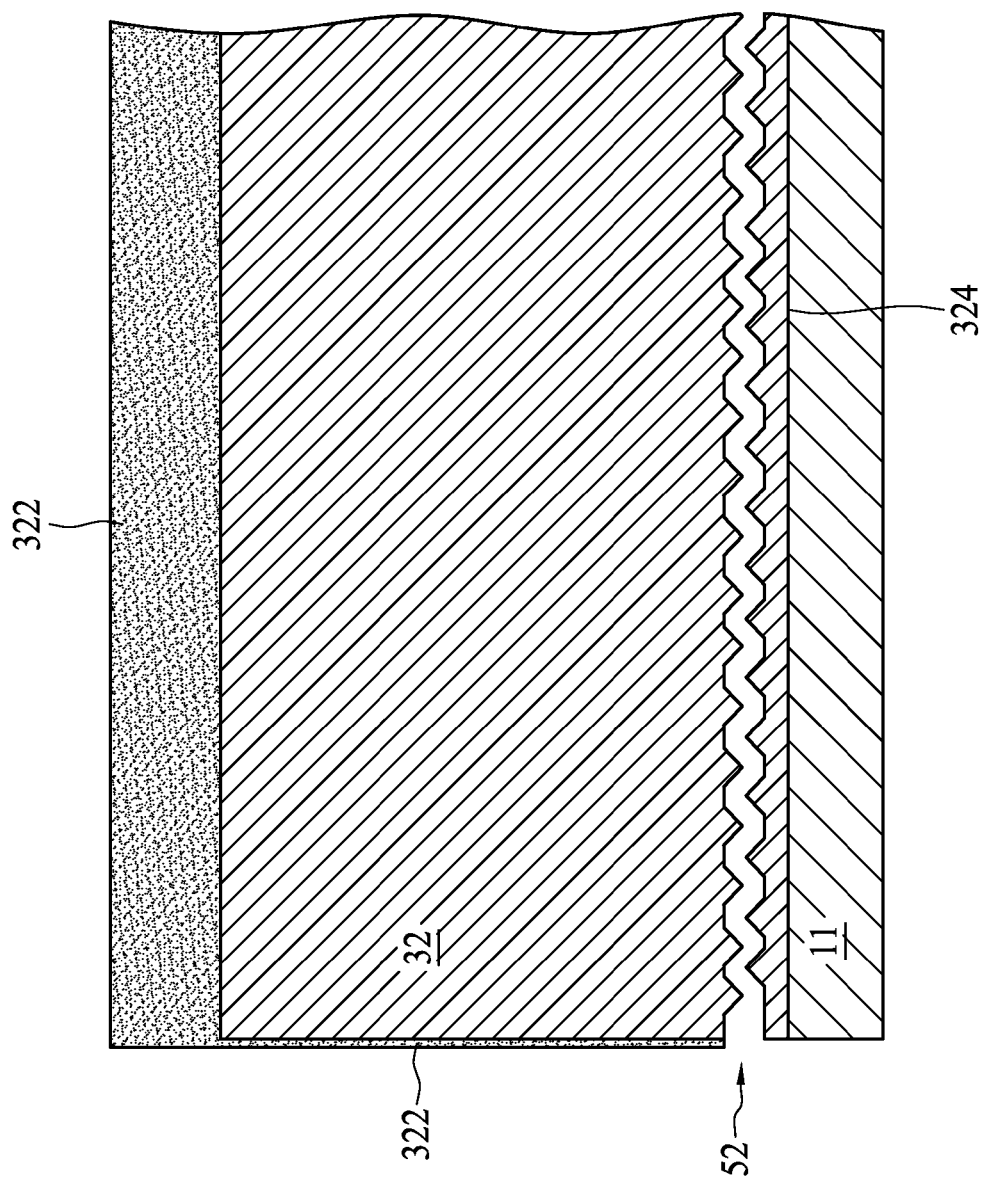


FIG. 11

500

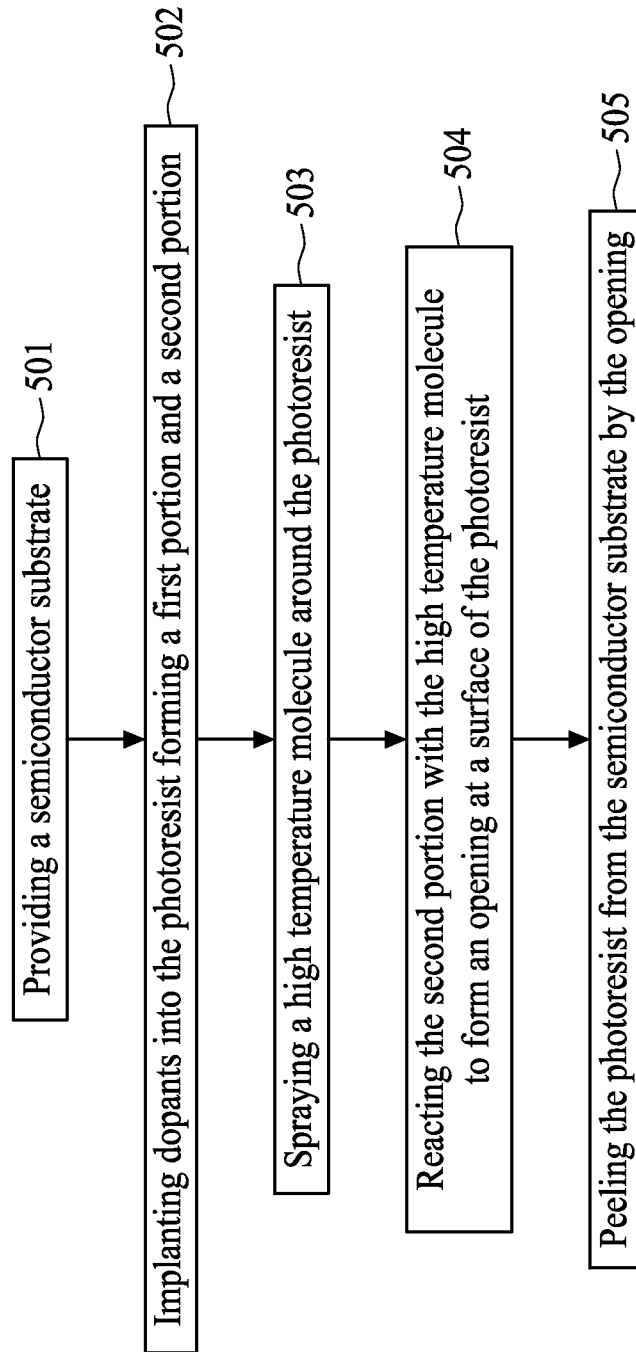


FIG. 12

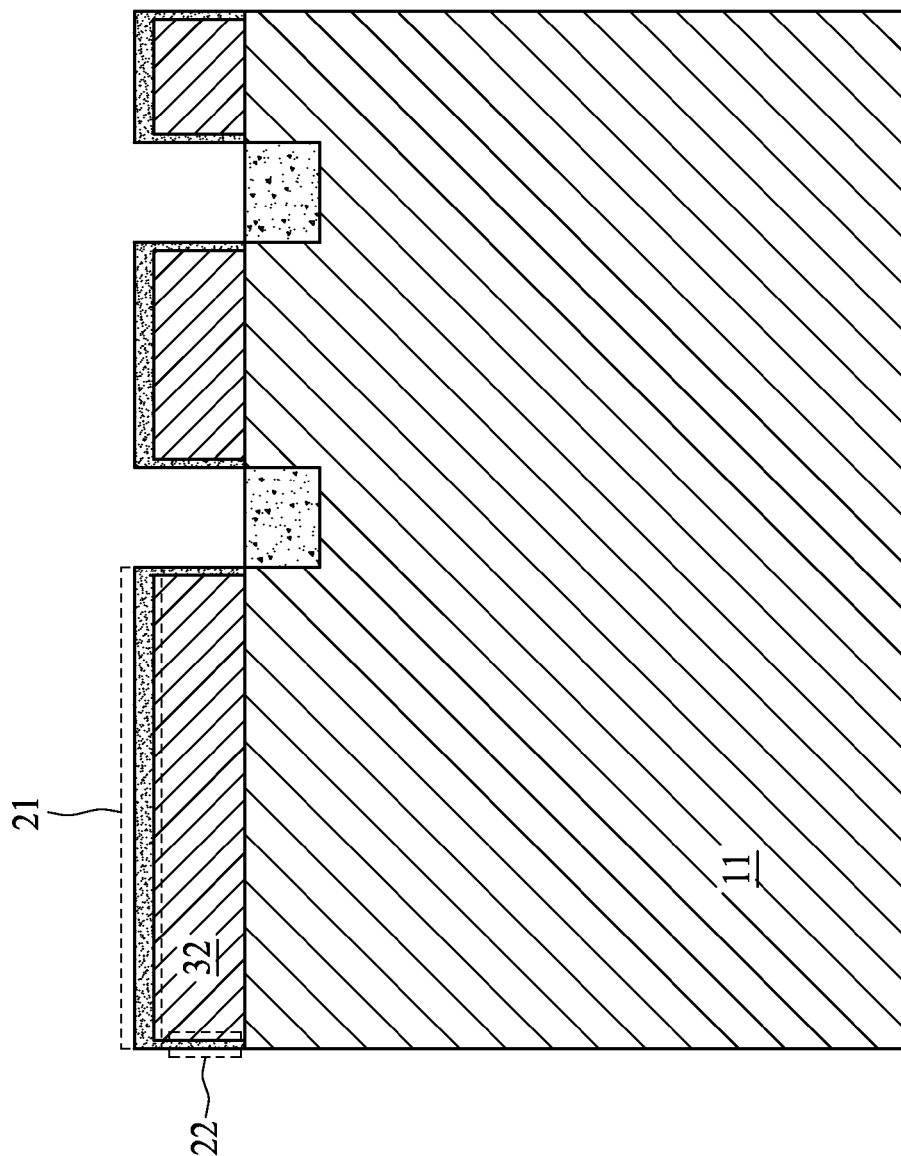


FIG. 13

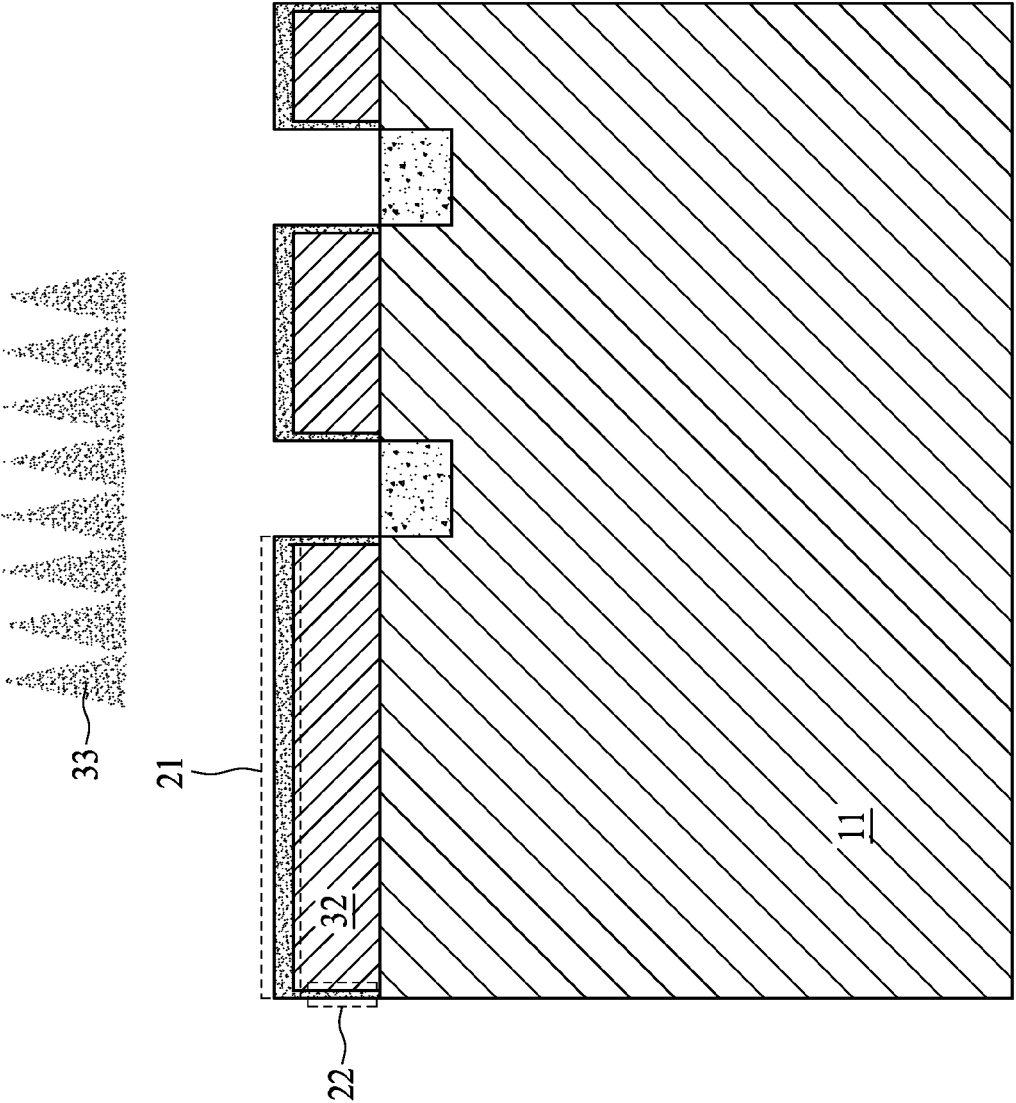


FIG. 14

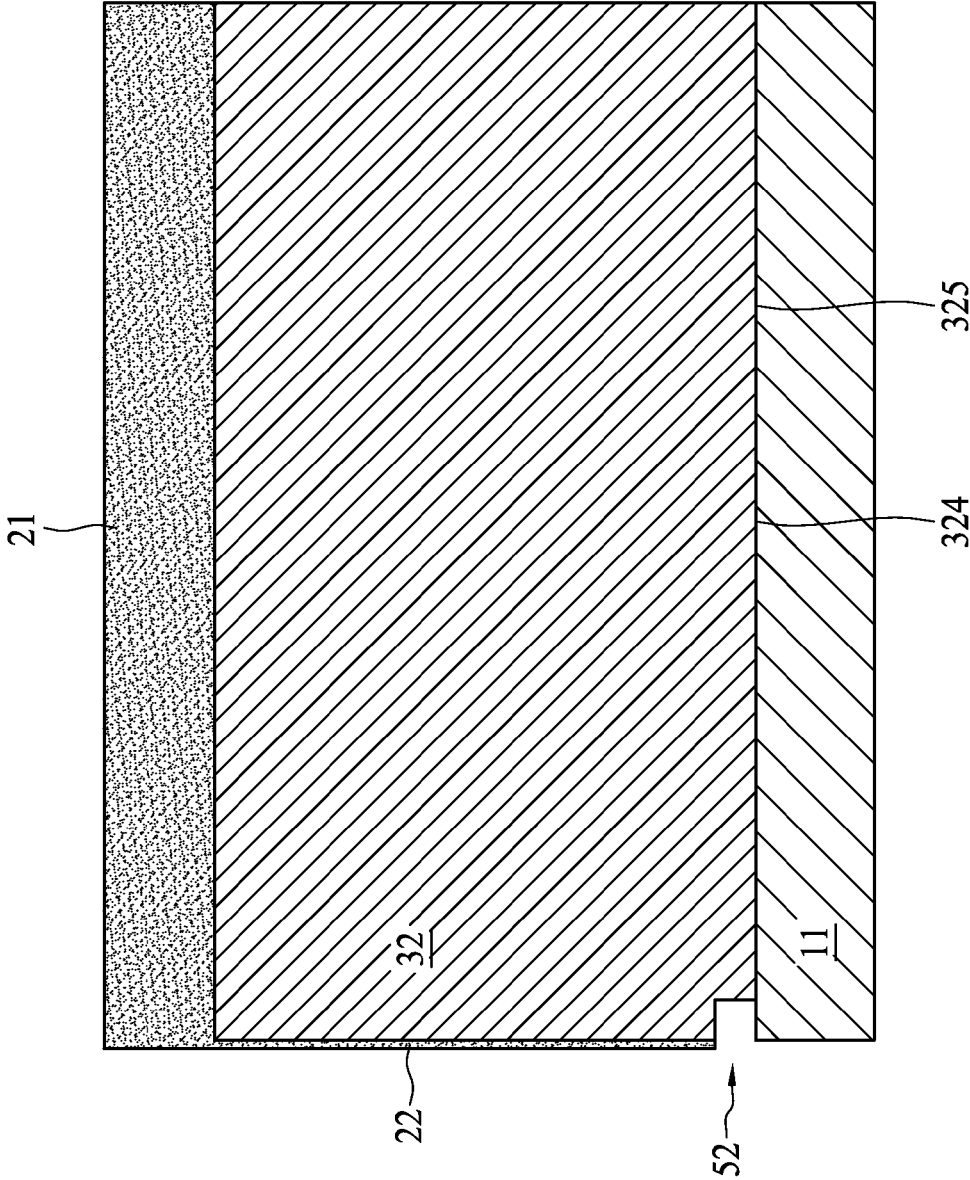


FIG. 15

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METHOD FOR SEMICONDUCTOR MANUFACTURING

FIELD

The disclosure relates to a method for manufacturing a semiconductor.

BACKGROUND

More than one million micro-electronic field effect transistors (e.g., complementary metal-oxide-semiconductor (CMOS) field effect transistors) are fabricated on a substrate (e.g., semiconductor wafer) to form an integrated circuit. During the fabrication process of the integrated circuit, a photoresist is deposited, exposed, and developed to create a mask utilized to etch the underlying layers.

To produce the integrated circuit, implanting ions into various portions of the integrated circuit is necessary. During ion implantation, wafers are bombarded by a beam of electrically charged ions, called dopants. Implantation changes the properties of the material where the dopants are implanted in order to achieve a particular electrical performance. These dopants are accelerated to an energy that will permit them to penetrate (i.e., implant) the film to a desired depth. During implantation, high-dose or high-energy ions may implant in the photoresist layer and cause a hard, crust-like layer to form on the surface of the photoresist layer. The crust layer is difficult to remove using conventional stripping processes. Moreover, if the crust layer or underlying photoresist is not removed, the residual photoresist becomes a contaminant during subsequent processes. Thus, an improved method for stripping a photoresist is still in great demand.

BRIEF DESCRIPTION OF THE DRAWINGS

Aspects of the present disclosure are best understood from the following detailed description when read with the accompanying figures. It is emphasized that, in accordance with the standard practice in the industry, various features are not drawn to scale. In fact, the dimensions of the various features may be arbitrarily increased or reduced for clarity of discussion.

A more complete understanding of the present disclosure may be derived by referring to the detailed description and claims when considered in connection with the Figures, where like reference numbers refer to similar elements throughout the Figures, and:

FIG. 1 is a top view of a system according to some embodiments of the present disclosure;

FIG. 2 is a cross-sectional view of a stripping chamber according to some embodiments of the present disclosure;

FIG. 3 is a cross-sectional view of a stripping chamber with a valve according to some embodiments of the present disclosure;

FIG. 4 is a flowchart of a method for decorticating the photoresist from the semiconductor substrate according to some embodiments of the present disclosure;

FIGS. 5 to 9 are cross-sectional views corresponding to various operations 301 to 307 in FIG. 4;

FIG. 10 is a flowchart of a method for separating the photoresist from the semiconductor substrate according to some embodiments of the present disclosure;

FIG. 11 is cross-sectional views corresponding to various operations 404 to 405 in FIG. 10;

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FIG. 12 is a flowchart of a method for peeling the photoresist from the semiconductor substrate according to some embodiments of the present disclosure; and

FIGS. 13 to 15 are cross-sectional views corresponding to various operations 502 to 505 in FIG. 12.

DETAILED DESCRIPTION OF THE INVENTION

The claimed subject matter is now described with reference to the drawings, wherein like reference numerals are generally used to refer to like elements throughout. In the following description, for purposes of explanation, numerous specific details are set forth in order to provide an understanding of the claimed subject matter. It is evident, however, that the claimed subject matter can be practiced without these specific details. In other instances, structures and devices are illustrated in block diagram form in order to facilitate describing the claimed subject matter.

In the present disclosure, a method for stripping a photoresist with a crust thereon from the semiconductor substrate is provided by using a stream of very small drops of liquid floating in the air. These small drops form a crack, a seam, an opening, or a hole at a bottom surface of the photoresist where it is less likely bombarded by implanting ions. The crack separates the photoresist having the crust thereon from the semiconductor substrate. Thus, the crust-like photoresist is stripped from the semiconductor substrate so as to avoid a contamination occurring at subsequent processes.

In various embodiments, these small drops perform the stripping function in the form of an etch steam, a sulfuric mist, or a high temperature molecule according to various designs. In some embodiments, the small drops form a steam with a sulfuric mixture, which etches a portion of the photoresist close to the interface between the photoresist and the semiconductor substrate such that several cracks or seams are formed around the interface. During the stripping process, a centrifugal force resulting from the spinning of the semiconductor substrate enlarges the cracks. After those cracks connect, the photoresist having the crust thereon is easily peeled from the semiconductor substrate so as to prevent the semiconductor substrate in the next run from the contaminant due to a crust-like photoresist.

In describing and claiming the present disclosure, the following terminology will be used in accordance with the definitions set forth below.

As used herein, a "substrate" refers to a bulk substrate on which various layers and device structure are formed. In some embodiments, the bulk substrate includes silicon or a compound semiconductor, such as Ga As, InP, Si/Ge, or SiC. Examples of the layers include dielectric layers, doped layers, polysilicon layers, or conductive layers. Examples of the device structures include transistors, resistors, and/or capacitors, which are interconnected through an interconnect layer to additional integrated circuits. In some embodiments, the bulk substrate includes a wafer such as a polished wafer, an epi wafer, an argon anneal wafer, a hai wafer and a silicon on insulator (SOI) wafer.

As used herein, a "semiconductor substrate" refers to a chip carrier, which is generally manufactured using two complex manufacturing processes, i.e., front-end manufacturing, and back-end manufacturing, each involving potentially hundreds of steps. Front-end manufacturing involves the formation of a plurality of die on the surface of a semiconductor wafer. Each die is typically identical and contains circuits formed by electrically connecting active and passive components. Back-end manufacturing involves singulating individual die from the finished wafer and packaging the die to

provide structural support and environmental isolation. Active electrical components, such as transistors, have the ability to control the flow of electrical current. Passive electrical components, such as capacitors, inductors, resistors, and transformers, create a relationship between voltage and current necessary to perform electrical circuit functions.

As used herein, “active and passive components” refers to components, which are formed on the surface of the semiconductor wafer by a series of process steps including doping, deposition, photolithography, etching, and planarization. Doping introduces impurities into the semiconductor material by techniques such as ion implantation or thermal diffusion. The doping process modifies the electrical conductivity of semiconductor material in active devices, transforming the semiconductor material into a permanent insulator, permanent conductor, or changing the way the semiconductor material changes in conductivity in response to an electric field. Transistors contain regions of varying types and degrees of doping arranged as necessary to enable the transistor to promote or restrict the flow of electrical current upon the application of an electric field.

Active and passive components are formed by layers of materials with different electrical properties. The layers are formed by a variety of deposition techniques determined in part by the type of material being deposited. For example, thin film deposition involves chemical vapor deposition (CVD), physical vapor deposition (PVD), electrolytic plating, and electroless plating processes. Each layer is generally patterned to form portions of active components, passive components, or electrical connections between components. The layers are patterned using photolithography, which involves the deposition of light sensitive material, e.g., photoresist, over the layer to be patterned. A pattern is transferred from a photomask to the photoresist using light. The portion of the photoresist pattern subjected to light is removed using a solvent, exposing portions of the underlying layer to be patterned. The remainder of the photoresist is removed, leaving behind a patterned layer. Alternatively, some types of materials are patterned by directly depositing the material into the areas or voids formed by a previous deposition/etch process using techniques such as electroless and electrolytic plating.

As used herein, “back-end manufacturing” refers to cutting or singulating the finished wafer into the individual die and then packaging the die for structural support and environmental isolation. To singulate the die, the wafer is scored and broken along non-functional regions of the wafer called saw streets or scribes. The wafer is singulated using a laser cutting device or saw blade. After singulation, the individual dies are mounted to a package substrate that includes pins or contact pads for interconnection with other system components. Contact pads formed over the semiconductor die are then connected to contact pads within the package. The electrical connections can be made with solder bumps, stud bumps, conductive paste, or wirebonds. An encapsulant or other molding material is deposited over the package to provide physical support and electrical isolation. The finished package is then inserted into an electrical system and the functionality of the semiconductor device is made available to the other system components.

As used herein, a “crust” or “crust layer” recited in the present disclosure is a layer formed on the photoresist when high dopant concentrations are implanted into the photoresist. The crust layer may form due to the photoresist losing hydrogen during the implantation. The loss of hydrogen from the surface of the photoresist layer promotes carbon bonding that creates a hard, graphite-like crust. In some embodiments, the stripped substrate is then annealed. By providing the

implantation, stripping, and annealing within a single system, oxidation of the semiconductor substrate is avoided while providing a high substrate throughput. The substrate throughput is increased because a portion of the dopant remains in the implantation chamber and is used during the implantation of the next photoresist. The portion of the dopant that remains in the implantation chamber reduces the amount of time necessary to perform the implantation for the next substrate.

As used herein, a “mask” or “mask layer” recited in the present disclosure is an object of a patterning operation. The patterning operation includes various steps and operations and varies in accordance with features of embodiments. In some embodiments, a patterning operation patterns an existing film or layer. The patterning operation includes forming a mask on the existing film or layer and removing the unmasked portion of the film or layer with an etch or other removal operation. The mask layer is a photoresist or a hardmask. In some embodiments, a patterning operation directly forms a patterned layer on a surface. The patterning operation includes forming a photosensitive film on the surface, conducting a photolithography operation and a developing operation. The remaining photosensitive film may be removed or retained and integrated into the package.

As used herein, a “Front Opening Universal Pod (FOUP)” recited in the present disclosure is a specialized plastic enclosure designed to hold silicon wafers securely and safely in a controlled environment, and to allow the wafers to be removed for processing or measurement by tools equipped with appropriate load ports and robotic handling systems. Each FOUP has various coupling plates, pins, and holes to allow the FOUP to be located on a load port, and to be manipulated by the AMHS (Automated Material Handling System). FOUPs may also contain RF tags that allow them to be identified by readers on tools.

In some embodiments as in FIG. 1, a system **100** according to the present disclosure is provided. The system **100** includes a transfer chamber **110** surrounded by three processing chambers **120**, **130** and **140**. A factory interface **210** is coupled to the transfer chamber **110** by a load lock chamber **220**. One or more FOUPs **230** are disposed in the factory interface **210** for storing substrate. A robot **150** is positioned in a central portion of the transfer chamber **110** to facilitate substrates to transfer among processing chambers **120**, **130**, **140** and the load lock chamber **220**. These FOUPs **230** are used to provide substrates into or to remove substrates from the system **100**. For instance, substrates are provided to the processing chambers **120**, **130** and **140** from one FOUP **230** through the load lock chamber **220** and removed from the system **100** through the load lock chamber **220** to another FOUP **230**.

Each of the processing chambers **120**, **130**, and **140** are configured to perform a different operation in processing of the substrate. In some embodiments, each of the processing chambers **120**, **130** and **140** is separately installed in a different tool or system. In some embodiments, the processing chamber **120** is an implantation chamber for implanting dopants into a workpiece. In certain embodiments, the implantation chamber is a P3i® chamber, available from Applied Materials, Inc. of Santa Clara, Calif. However, other suitable implantation chambers, including those produced by other manufacturers, are utilized as well.

In some embodiments, the processing chamber **140** is an annealing chamber that is utilized to anneal the workpiece after implanting or stripping. In certain embodiments, the annealing chamber is a Radiance® rapid thermal processing chamber, available from Applied Materials, Inc. However, other suitable chambers, including those produced by other manufacturers are utilized as well.

In some embodiments, the processing chamber **130** is configured as a stripping chamber and is utilized to strip the photoresist having the crust thereon from the workpiece. In certain embodiments, the stripping chamber **131** described in FIG. **2** includes a chamber body **132**, a chuck **133**, a spray bar **134** and a mixer **151**. The workpiece **135** or the semiconductor substrate is positioned on the chuck **133**, which is accommodated in the chamber body **132**. The mixer **151** is used to stir sulfuric mixtures and a steam to form a sulfuric mist **136**. The spray bar **134** is designed to transfer the sulfuric mist **136** into the chamber body **132** and to distribute the sulfuric mist **136** around the workpiece **135**. However, other suitable stripping chambers, including those produced by other manufacturers, are utilized as well. In certain embodiments, the spray bar **134** has several nozzles **240**, which is used to spray the sulfuric mist **136** in a line from a center of the semiconductor substrate **11** to an edge of the semiconductor substrate **11**.

In still other embodiments, the stripping chamber **231** configured as in FIG. **3** includes a sulfuric mist source **137**, a valve **138** and an exit port **139**, as well as the chamber body **132** and the chuck **133** previously discussed with reference thereto and are not repeated here for simplicity. The sulfuric mist source **137** is designed to feed the sulfuric mist **136** into the stripping chamber **231**. The valve **138** is used for the sulfuric mist **136** to exit the stripping chamber **231** through the exit port **139**.

A method of fabricating a semiconductor device is used to strip or peel the photoresist having the crust layer thereon so as to prevent contaminants, due to the crust layer, from contaminating subsequent processes. The method includes a number of operations and the description and illustrations are not deemed as a limitation as the order of the operations.

A term "inserting" or "inserted" is used in the present disclosure to describe an operation of incorporating an impurity into an object. The inserting operation includes various steps and processes and varies in accordance with the features of embodiments. In certain embodiments, the inserting operation includes ion-implanting the dopants into the object. In some embodiments, the inserting operation includes pre-depositing the dopants into the object. For instance, the pre-deposition uses boron-based gas, such as B_2H_6 or BCl_3 , within a temperature from about $1000^\circ C.$ to about $1200^\circ C.$, within about 200 sec to about 400 sec (about 50 CC to about 100 CC) for forming a p-well or a p-n junction string formation in an n-type semiconductor substrate. In some embodiments, the pre-deposition uses phosphorus-based gas, such as PH_3 or $POCl_3$, within a temperature from about $1000^\circ C.$ to about $1200^\circ C.$, within about 200 sec to about 400 sec (about 50 CC to about 100 CC) for forming an n-well or a p-n junction string formation in a p-type semiconductor substrate. In the present disclosure, a high and a low temperature are traded off for a short duration and a long duration for the operation, respectively.

A term "spraying" or "sprayed" is used in the present disclosure to describe an operation of putting a stream of very small drops of liquid on an object. The spraying operation includes various steps and processes and varies in accordance with the features of embodiments. In some embodiments, the spraying operation includes heating a stream of very small drops of liquid to a temperature range between about $80^\circ C.$ and about $200^\circ C.$

A term "decorticating" or "decorticated" is used in the present disclosure to describe an operation of removing the outer coverings from an object. The decorticating operation includes various steps and processes and varies in accordance

with the features of embodiments. In some embodiments, the decorticating operation includes enlarging or connecting the cracks in the photoresist.

FIG. **4** is a diagram of a method **300** for decorticating a photoresist having a carbonized photoresist thereon from a semiconductor structure in accordance with some embodiments of the present disclosure. The method **300** includes several operations, which are discussed in detail with reference to FIGS. **5** to **9**. At operation **301**, a semiconductor substrate is provided. At operation **302**, a photoresist is formed on the semiconductor substrate. At operation **303**, dopants are inserted into the photoresist to carbonize a portion of the photoresist. At operation **304**, an etch steam is sprayed around the photoresist. At operation **305**, a hole is formed at a surface of the photoresist by the etch steam. At operation **306**, the etch steam is flowed into the hole so as to remove a portion of the photoresist at an interface between the semiconductor substrate and the photoresist. At operation **307**, the photoresist is decorticated from the semiconductor substrate.

FIGS. **5** to **9** have been simplified for a better understanding of the inventive concepts of the present disclosure. In FIGS. **5** to **9**, elements with same labeling numbers as those in FIGS. **1** to **3** are previously discussed with reference thereto and are not repeated here for simplicity.

Referring to FIG. **5**, a semiconductor substrate **11** is provided. In some embodiments, the semiconductor substrate **11** is a wafer including several dies, where each of which has active and passive devices using semiconductor manufacturing processes described above.

Referring to FIG. **6**, the photoresist **32** is formed on the semiconductor substrate **11**. In some embodiments as shown in FIG. **6**, after the photoresist **32** is attached on the top surface of the semiconductor substrate **11**, a portion of the photoresist **32** is removed by a developing process to form a gap **321** and further expose the top surface of the semiconductor substrate **11**.

Referring to FIG. **7**, during the implantation operation in the implantation chamber, dopants are inserted into the photoresist **32** to change chemical properties thereof. A high concentration of dopants promotes carbonization of a portion **322** of the photoresist **32**. Since the implanting is beaming from top of the semiconductor substrate **11**, the upper photoresist **32** is more likely carbonized than a lateral photoresist **32**. That is, the concentration of dopants in the upper photoresist **32** is higher than those in the lateral photoresist **32**. In some embodiments, the dopant concentration of the portion **322** is between about 1×10^{13} and about 1×10^{16} . In certain embodiments, the concentration of dopants is between about 3×10^{13} and about 8×10^{16} . In other embodiments, the concentration of dopants is between about 7×10^{14} and about 6×10^{17} . In still some embodiments, the predetermined concentration is between about 9×10^{12} and about 4×10^{18} .

In FIG. **7**, dopants are inserted into the semiconductor substrate **11** to form the doped region **310**, which is a p-well region, an n-well region, an LDD region, a source region, or a drain region according to the desired performance. Based on the desired electrical properties, the dopant is selected from group III elements (e.g., Gallium), group IV elements (e.g., Germanium), and group V elements (e.g., Arsenic).

Referring to FIG. **8**, the semiconductor substrate **11** having a crust-like photoresist **32** thereon is transferred from the implantation chamber to the stripping chamber. In a stripping operation, an etch steam **34** is sprayed into the stripping chamber so as to allow small drops of liquid of the etch steam **34** to float in the air around the photoresist **32**. The temperature of the etch steam **34** is heated between about $150^\circ C.$ and

about 200° C. In some embodiments, the temperature of the etch steam **34** is between about 75° C. and about 185° C. In certain embodiments, the temperature of the etch steam **34** is between about 92° C. and about 225° C. In still some embodiments, the temperature of the etch steam **34** is between about 145° C. and about 175° C. In certain embodiments, a high and a low temperature are traded off for a short duration and a long duration for the operation, respectively.

In some embodiments, those small drops of liquid in the etch steam **34** are mixtures of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2). The mixtures transiently form atomic oxygen, which attacks surface carbons of the photoresist and the stable carbonized crust to form carbon dioxide (CO_2) so as to dissolve the photoresist and the stable carbonized crust. In certain embodiments, the etch steam **34** is selected from peroxymonosulfuric acid (H_2SO_5), peroxydisulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$), a mixture of ozonated water, sulfur containing solutions, chlorine containing solutions, a base piranha (a mixture of ammonium hydroxide (NH_4OH) with hydrogen peroxide), a mixture of ammonium hydroxide, hydrogen peroxide and water (H_2O), a mixture of water and hydrogen fluoride (HF), a mixture of hydrogen fluoride, ammonium fluoride (NH_4F) and water, and a mixture of hydrogen chloride (HCl), water and hydrogen peroxide.

In some embodiments, the pressure in the stripping chamber affects the uniformity of those small drops of liquid in the etch steam **34**. The desired pressure for uniformity is between about 14.7 psi and about 29.4 psi. In certain embodiments, the pressure is between about 11.3 psi and about 32.6 psi. In other embodiments, the pressure is between about 17.6 psi and about 42.7 psi. In still some embodiments, the pressure is between about 9.6 psi and about 38.7 psi.

In some embodiments, the speed of flowing the etch steam **34** into the stripping chamber affects the duration of the stripping operation. The desired speed is between about $0.02 \text{ m}^3 \cdot \text{s}^{-1}$ and about $1.25 \text{ m}^3 \cdot \text{s}^{-1}$. In certain embodiments, the speed is between about $0.05 \text{ m}^3 \cdot \text{s}^{-1}$ and about $2.61 \text{ m}^3 \cdot \text{s}^{-1}$. In other embodiments, the speed is between about $0.15 \text{ m}^3 \cdot \text{s}^{-1}$ and about $1.85 \text{ m}^3 \cdot \text{s}^{-1}$. In still some embodiments, the speed is between about $0.37 \text{ m}^3 \cdot \text{s}^{-1}$ and about $3.91 \text{ m}^3 \cdot \text{s}^{-1}$.

In the stripping operation as in FIG. 8, dissolving a part of the photoresist **32** by using the etch steam **34** leaves a hole **51** at a surface **323** of the photoresist **32** as shown in FIG. 9. FIG. 9 is an enlarged view of FIG. 8. In FIG. 9, the previously discussed pressure drives the etch steam **34** to flow into the hole **51** so as to further remove or dissolve a portion of the photoresist **32** so as to enlarge the hole **51**. In some embodiments, the portion of the photoresist **32** is located near an interface **324** between the semiconductor substrate **11** and the photoresist **32**. There are several holes **51** formed around the photoresist **32**. As the etch steam **34** further invades the photoresist **32**, the holes **51** enlarge and extend so as to connect with each other. When the different holes **51** are connected, the photoresist **32** is divided into two parts. The upper part having the crust layer is easily removed by the centrifugal force, while the bottom part without the crust layer is further dissolved by the etch steam **34**. The photoresist **32** is efficiently decorticated from the semiconductor substrate **11** without a residual photoresist. Therefore, the present disclosure provides a full-wet approach, which no plasma ash process is involved in and hence saves the costs of the ash process apparatus and the relevant consumables thereof is available.

FIG. 10 is a diagram of a method **400** for separating a photoresist having a carbonized photoresist thereon from a semiconductor structure in accordance with some embodiments of the present disclosure. The method **400** includes several operations, which are discussed in detail with refer-

ence to FIG. 11. At operation **401**, a sulfuric mist is formed. At operation **402**, the sulfuric mist is transferred into the spray bar. At operation **403**, the sulfuric mist is distributed around the carbonized photoresist. At operation **404**, a crack is formed at a surface of the photoresist by the sulfuric mist, wherein the crack is located near an interface between a semiconductor substrate and the photoresist. At operation **405**, the photoresist is separated from the semiconductor substrate by the crack.

FIG. 11 has been simplified for a better understanding of the inventive concepts of the present disclosure. In FIG. 11, elements with same labeling numbers as those in FIG. 2 are previously discussed with reference thereto and are not repeated here for simplicity.

Referring back to FIG. 2, during the stripping operation, the sulfuric mist **136** is formed in the mixer **51**, which transfers the sulfuric mist **136** into the spray bar **134**. The spray bar **134** sprays or distributes the sulfuric mist **136** above the workpiece **135**, which may be a semiconductor substrate **11** with carbonized photoresist **32** formed thereon as previously discussed. The sulfuric mist **136** dissolves the photoresist **32** to form a crack **52** in the photoresist **32** shown in FIG. 11. Because the photoresist **32** is exposed under the sulfuric mist **136**, several cracks on different sides are formed on the outer surface of the photoresist **32** by the sulfuric mist. In some embodiments of the stripping operation, the cracks **52** are located near the interface **324** between the semiconductor substrate **11** and the photoresist **32**. When the cracks **52** extend into the bottom surface of the photoresist **32** and finally connect together, the photoresist **32** having the carbonized part thereon is separated from the semiconductor substrate **11**. Consequently, the residue of photoresist **32** is quickly cleaned or dissolved by the sulfuric mist **136**. Thus, there is no contaminant to the subsequent process that is sourced from the residual photoresist being generated atop the semiconductor substrate **11**.

In some embodiments, since the spray bar **134** is adjustable to swiveling or spinning over the semiconductor substrate **11** and the semiconductor substrate **11** is spun on the chuck **133**, the sulfuric mist **136** quickly dissolves the photoresist **32** to form a jagged crack **52** in FIG. 11. The swiveling frequency of the spray bar **134** is adjustable between about 150 rpm and about 1500 rpm. In some embodiments, the swiveling frequency is between about 195 rpm and about 2100 rpm. In certain embodiments, the swiveling frequency is between about 255 rpm and about 4500 rpm. In still some embodiments, the swiveling frequency is between about 450 rpm and about 6700 rpm.

In some embodiments, the temperature of the sulfuric mist **136** is heated between about 160° C. and about 205° C. In some embodiments, the temperature of the sulfuric mist **136** is between about 85° C. and about 195° C. In certain embodiments, the temperature of the sulfuric mist **136** is between about 112° C. and about 275° C. In still some embodiments, the temperature of the sulfuric mist **136** is between about 195° C. and about 325° C. In some embodiments, a high and a low temperature are traded off for a short duration and a long duration for the operation, respectively.

In some embodiments, the small drops of liquid in the sulfuric mist **136** are peroxymonosulfuric acid (H_2SO_5). The mixtures transiently form atomic oxygen, which attacks surface carbons of the photoresist and the stable carbonized crust to form carbon dioxide (CO_2) so as to dissolve the photoresist and the stable carbonized crust. In certain embodiments, the etch steam **34** is selected from peroxydisulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$), a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2), a mixture of ozonated water, sulfur contain-

ing solutions, chlorine containing solutions, a base piranha (a mixture of ammonium hydroxide (NH_4OH) with hydrogen peroxide), a mixture of ammonium hydroxide, hydrogen peroxide and water (H_2O), a mixture of water and hydrogen fluoride (HF), a mixture of hydrogen fluoride, ammonium fluoride (NH_4F) and water, and a mixture of hydrogen chloride (HCl), water and hydrogen peroxide.

In some embodiments, the pressure in the stripping chamber for the stripping operation affects the uniformity of those small drops of liquid in the sulfuric mist **136**. The desired pressure for uniformity is between about 15.7 psi and about 28.4 psi. In certain embodiments, the pressure is between about 10.3 psi and about 33.6 psi. In other embodiments, the pressure is between about 18.6 psi and about 45.7 psi. In still some embodiments, the pressure is between about 7.6 psi and about 68.7 psi.

In some embodiments, the speed of flowing the sulfuric mist **136** into the stripping chamber affects the duration of the stripping operation. The desired speed is between about $0.01 \text{ m}^3 \cdot \text{s}^{-1}$ and about $1.85 \text{ m}^3 \cdot \text{s}^{-1}$. In certain embodiments, the speed is between about $0.07 \text{ m}^3 \cdot \text{s}^{-1}$ and about $3.61 \text{ m}^3 \cdot \text{s}^{-1}$. In other embodiments, the speed is between about $0.55 \text{ m}^3 \cdot \text{s}^{-1}$ and about $1.95 \text{ m}^3 \cdot \text{s}^{-1}$. In still some embodiments, the speed is between about $0.77 \text{ m}^3 \cdot \text{s}^{-1}$ and about $5.91 \text{ m}^3 \cdot \text{s}^{-1}$.

FIG. **12** is a diagram of a method **500** for peeling a photoresist from a semiconductor structure in accordance with some embodiments of the present disclosure. The method **500** includes several operations, which are discussed in detail with reference to FIGS. **13** to **15**. At operation **501**, a semiconductor substrate having a photoresist thereon is provided. At operation **502**, dopants are implanted into the photoresist that causes the photoresist to form a first portion and a second portion, wherein a dopant concentration of the first portion is greater than a dopant concentration of the second portion. At operation **503**, a high temperature molecule is sprayed around the photoresist. At operation **504**, the second portion is reacted with the high temperature molecule to form an opening at a surface of the photoresist, wherein the surface attaches to an interface between the semiconductor substrate and the photoresist. At operation **505**, the photoresist is peeled from the semiconductor substrate by the opening.

FIGS. **13** to **15** have been simplified for a better understanding of the inventive concepts of the present disclosure. In FIGS. **13** to **15**, elements with the same labeling numbers as those in FIGS. **1** to **12** are previously discussed with reference thereto and are not repeated here for simplicity.

Referring to FIG. **13**, during the implantation operation, dopants are inserted into the first portion **21** of the photoresist **32** and the second portion **22** of the photoresist **32**. Since the implanting is beaming above the semiconductor substrate **11**, the dopant concentration on the first portion **21** is greater than the concentration of the second portion **22**. Therefore, the first portion **21** is heavily carbonized. In some embodiments, the dopant concentration of the first portion **21** is between about 1.5×10^{13} and about 2.1×10^{16} . In certain embodiments, the dopant concentration of the first portion **21** is between about 3.5×10^{13} and about 8.6×10^{16} . In other embodiments, the dopant concentration of the first portion **21** is between about 7.6×10^{14} and about 6.9×10^{17} . In still some embodiments, the dopant concentration of the first portion **21** is between about 9.2×10^{12} and about 4.8×10^{18} .

After the implantation operation, the semiconductor substrate **11** is transferred to perform the stripping operation in the stripping chamber. Referring to FIG. **14**, a high temperature molecule **33** is sprayed in the form of small drops of liquid to float in the air around the photoresist **32**. The temperature of the high temperature molecule **33** is adjusted

between about 155°C . and about 235°C . In some embodiments, the temperature of the high temperature molecule **33** is between about 55°C . and about 285°C . In certain embodiments, the temperature of the high temperature molecule **33** is between about 132°C . and about 325°C . In still some embodiments, the temperature of the high temperature molecule **33** is between about 345°C . and about 575°C . In certain embodiments, a high and a low temperature are traded off for a short duration and a long duration for the operation, respectively.

In some embodiments, those small drops of liquid in the etch steam **34** are peroxydisulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$). The mixtures transiently form atomic oxygen, which attacks surface carbons of the photoresist and the stable carbonized crust to form carbon dioxide (CO_2) so as to dissolve the photoresist and the stable carbonized crust. In certain embodiments, the etch steam **34** is selected from peroxymonosulfuric acid (H_2SO_5), a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2), a mixture of ozonated water, sulfur containing solutions, chlorine containing solutions, a base piranha (a mixture of ammonium hydroxide (NH_4OH) with hydrogen peroxide), a mixture of ammonium hydroxide, hydrogen peroxide and water (H_2O), a mixture of water and hydrogen fluoride (HF), a mixture of hydrogen fluoride, ammonium fluoride (NH_4F) and water, and a mixture of hydrogen chloride (HCl), water and hydrogen peroxide.

In some embodiments, the pressure in the stripping chamber affects the uniformity of the small drops of liquid in the high temperature molecule **33**. The desired pressure for uniformity is between about 10.7 psi and about 20.4 psi. In certain embodiments, the pressure is between about 16.3 psi and about 62.6 psi. In other embodiments, the pressure is between about 37.6 psi and about 92.7 psi. In still some embodiments, the pressure is between about 59.6 psi and about 138.7 psi.

In some embodiments, the speed of flowing the high temperature molecule **33** into the stripping chamber affects the duration of the stripping operation. The desired speed is between about $0.09 \text{ m}^3 \cdot \text{s}^{-1}$ and about $2.35 \text{ m}^3 \cdot \text{s}^{-1}$. In certain embodiments, the speed is between about $0.18 \text{ m}^3 \cdot \text{s}^{-1}$ and about $4.67 \text{ m}^3 \cdot \text{s}^{-1}$. In other embodiments, the speed is between about $0.95 \text{ m}^3 \cdot \text{s}^{-1}$ and about $8.85 \text{ m}^3 \cdot \text{s}^{-1}$. In still some embodiments, the speed is between about $1.37 \text{ m}^3 \cdot \text{s}^{-1}$ and about $13.91 \text{ m}^3 \cdot \text{s}^{-1}$.

In the stripping operation as in FIG. **15**, when the high temperature molecule **33** is reacted with a part of the second portion **22**, the opening **53** is formed at the surface **325** of the photoresist **32**. The surface **325** attaches to the interface **324** between the semiconductor substrate **11** and the photoresist **32**. As the high temperature molecule **33** further invades the photoresist **32**, the openings **53** enlarge and extend so as to connect with each other. After the openings **53** connect with each other, the photoresist **32** is completely peeled from the semiconductor substrate **11**. Therefore, no residual photoresist **32** remains on the top surface of the semiconductor substrate **11**.

In some embodiments, a method for decorticating a photoresist includes providing a semiconductor substrate. The method also includes forming a photoresist on the semiconductor substrate. The method also includes inserting dopants into the photoresist with a predetermined concentration to carbonize a portion of the photoresist. The method also includes spraying an etch steam around the photoresist. The method also includes forming a hole at a surface of the photoresist by the etch steam. The method also includes flowing the etch steam into the hole and further removing a portion of the photoresist near an interface between the semiconductor

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substrate and the photoresist. The method also includes decorticating the photoresist from the semiconductor substrate.

In some embodiments, a method for separating a photoresist includes forming a sulfuric mist. The method also includes transferring the sulfuric mist into the spray bar. The method also includes distributing the sulfuric mist around a carbonized photoresist. The method also includes forming a crack at a surface of the photoresist by the sulfuric mist, wherein the crack is located near an interface between a semiconductor substrate and the photoresist. The method also includes separating the photoresist from the semiconductor substrate by the crack.

In some embodiments, a method for peeling a photoresist includes providing a semiconductor substrate wherein a photoresist is formed above the semiconductor substrate. The method also includes implanting dopants into the photoresist forming a first portion and a second portion, wherein a dopant concentration of the first portion is greater than a dopant concentration of the second portion and the first portion is carbonized. The method also includes spraying a high temperature molecule around the photoresist. The method also includes reacting the second portion with the high temperature molecule to form an opening at a surface of the photoresist, wherein the surface attaches to an interface between the semiconductor substrate and the photoresist. The method also includes peeling the photoresist from the semiconductor substrate by the opening.

Although the subject matter has been described in language specific to structural features or methodological acts, it is to be understood that the subject matter of the appended claims is not necessarily limited to the specific features or acts described above. Rather, the specific features and acts described above are disclosed as example forms of implementing the claims.

Various operations of embodiments are provided herein. The order in which some or all of the operations are described should not be construed as to imply that these operations are necessarily order dependent. Alternative ordering will be appreciated by one skilled in the art having the benefit of this description. Further, it will be understood that not all operations are necessarily present in each embodiment provided herein. It will be appreciated that layers, features, elements, etc. depicted herein are illustrated with particular dimensions relative to one another, such as structural dimensions or orientations, for example, for purposes of simplicity and ease of understanding and that actual dimensions of the same differ substantially from that illustrated herein, in some embodiments.

Further, unless specified otherwise, “first,” “second,” or the like are not intended to imply a temporal aspect, a spatial aspect, an ordering, etc. Rather, such terms are merely used as identifiers, names, etc. for features, elements, items, etc. For example, a first channel and a second channel generally correspond to channel A and channel B or two different or two identical channels or the same channel.

As used in this application, “or” is intended to mean an inclusive “or” rather than an exclusive “or.” In addition, “a” and “an” as used in this application are generally to be construed to mean “one or more” unless specified otherwise or clear from context to be directed to a singular form. Furthermore, to the extent that “includes,” “having,” “has,” “with,” or variants thereof are used in either the detailed description or the claims, such terms are intended to be inclusive in a manner similar to “comprising”.

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What is claimed is:

1. A method, comprising:

providing a semiconductor substrate;

forming a photoresist on the semiconductor substrate;

inserting dopants into the photoresist with a predetermined concentration to carbonize the photoresist to make a dopant concentration of a first portion of the photoresist is greater than a dopant concentration of a second portion of the photoresist;

spraying an etch steam around the photoresist;

forming a hole at a surface of the second portion of the photoresist by the etch steam;

flowing the etch steam into the hole and further removing a portion of the photoresist near an interface between the semiconductor substrate and the photoresist; and decorticating the photoresist from the semiconductor substrate.

2. The method of claim 1, wherein the semiconductor substrate includes a doped region selected from a p-well region, an n-well region, a source region, and a drain region.

3. The method of claim 1, wherein a temperature range of the etch steam is between about 150° C. and 200° C.

4. The method of claim 1, wherein the etch steam includes a mixture of sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂).

5. The method of claim 1, wherein the predetermined concentration is between about 1×10¹³ and about 1×10¹⁶.

6. The method of claim 1, wherein spraying the etch steam to surround the photoresist is under a pressure between about 9.6 psi and about 42.7 psi.

7. The method of claim 1, wherein spraying the etch steam to surround the photoresist is at a flowing speed between about 0.02 m³·s⁻¹ and about 3.91 m³·s⁻¹.

8. A method, comprising:

forming a sulfuric mist;

transferring the sulfuric mist into a spray bar;

distributing the sulfuric mist around a carbonized photoresist, wherein the carbonized photoresist comprises a first portion and a second portion, and a dopant concentration of the first portion is greater than a dopant concentration of the second portion;

forming a crack at a surface of the second portion of the photoresist by the sulfuric mist, wherein the crack is located near an interface between a semiconductor substrate and the photoresist; and separating the photoresist from the semiconductor substrate by the crack.

9. The method of claim 8, wherein the sulfuric mist has a temperature between about 150° C. and 200° C.

10. The method of claim 8, wherein the spray bar has a plurality of nozzles, and the nozzles spray the sulfuric mist in a line from a center of the semiconductor substrate to an edge of the semiconductor substrate.

11. The method of claim 8, further comprising spinning the semiconductor substrate to allow the sulfuric mist to cover the photoresist.

12. The method of claim 8, further comprising swiveling the spray bar over the semiconductor substrate.

13. The method of claim 12, wherein the swiveling frequency is between about 150 rpm and about 6700 rpm.

14. The method of claim 8, wherein distributing the sulfuric mist to surround the photoresist is under a pressure between about 7.6 psi and about 68.7 psi.

15. The method of claim 8, wherein distributing the sulfuric mist to surround the photoresist is at a flowing speed between about 0.01 m³·s⁻¹ and about 5.91 m³·s⁻¹.

16. A method, comprising:
 providing a semiconductor substrate wherein a photoresist
 is formed above the semiconductor substrate;
 implanting dopants into the photoresist forming a first por-
 tion and a second portion, wherein a dopant concentra- 5
 tion of the first portion is greater than a dopant concentra-
 tion of the second portion and the first portion is
 carbonized;
 spraying a high temperature molecule around the photore-
 sist; 10
 reacting the second portion with a high temperature mol-
 ecule to form an opening at a surface of the second
 portion of the photoresist, wherein the surface attaches
 to an interface between the semiconductor substrate and
 the photoresist; and 15
 peeling the photoresist from the semiconductor substrate
 by the opening.
17. The method of claim 16, wherein the dopant concen-
 tration of the first portion is between about 1×10^{13} and about
 1×10^{16} . 20
18. The method of claim 16, wherein spraying a high
 temperature molecule to surround the photoresist is under a
 pressure between about 10.7 psi and about 138.7 psi.
19. The method of claim 16, wherein the high temperature
 molecule includes a peroxy monosulfuric acid (H_2SO_5). 25
20. The method of claim 16, wherein spraying a high
 temperature molecule to surround the photoresist is at an
 injection speed between about $0.09 \text{ m}^3 \cdot \text{s}^{-1}$ and about 13.91
 $\text{m}^3 \cdot \text{s}^{-1}$.

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